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LASER TEMPERATURE-JUMP KINETIC STUDIES OF FAST REACTIONS

IN NONAQUEOUS SOLUTIONS

Edward M. Eyring, Principal Investigator

Department of Chemistry

University of Utah

Salt Lake City, Utah 84112

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>Ultrasonic absorption methods have elucidated the kinetics of complexation of lithium ions by cyclic and acyclic polyethers in nonaqueous solvents. The interaction between the cation and polyether chain is localized and does not depend on chain length. Stability constants for lithium-ion-crown-ether complexes in a room temperature molten salt have been determined by lithium-7 nmr. Error estimation using the sequential simplex method in nonlinear curve-fitting has been demonstrated on small computers.</p> | | | | |
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Laser Temperature-Jump Kinetic Studies of Fast
Reactions in Nonaqueous Solutions

(Final Report)

Model systems for two different types of lithium battery electrolytes have been examined with ultrasonic absorption and nuclear magnetic resonance techniques. The rate of complexation of lithium ion by the macrocyclic polyether 18-crown-6 in dry propylene carbonate was successfully analyzed¹ in terms of two high frequency relaxation processes involving the stepwise desolvation of the lithium ion. Comparisons were made between 18-crown-6 and several nitrogen heterocyclic ligands in a subsequent paper.² Ethylene oxide oligomers were explored kinetically as ligands for Li^+ in dry acetonitrile in what one referee said "is a massive paper which adds significantly to our understanding of the dynamics of poly(ether) coordination." The most interesting generalization to emerge from this work is that the cation-polyether interaction is a localized one that is independent of the length of the poly(ethylene oxide) chain at least up to an average molar mass of 15,000.

A parallel study⁴ of lithium ion complexation by crown ethers in a room temperature molten salt (the binary AlCl_3 -1-methyl-3-ethylimidazolium chloride melt) has been carried out by lithium-7 nmr. The objective was the determination of stability constants between Li^+ and four crown ethers. In order of increasing complex ion stability the ligands are 18-crown-6 < 12-crown-4 < benzo-15-crown-5 < 15-crown-5. Stability constant data for the Li^+ -15-crown-5 complex were obtained over a range of temperatures thus permitting a determination also of ΔH and ΔS for the formation of this complex.

An investigation⁵ of error estimation using the sequential simplex method was carried out. An expert in the field subsequently made the following assessment⁶ of this paper: "The simplex method is used extensively in nonlinear curve-fitting applications. The present study [Phillips and Eyring, 1988] reports an advance that will be extremely useful in this context. Incorporation of this approach into nonlinear curve-fitting routines would be quite a step forward in the production of realistic values for fitted parameters along with the estimates of their errors. The major implication of this work is that there is now no reason to settle for parameter estimates without accompanying error estimates, even from statistical programs running on very small machines. There is essentially no penalty for evaluating the error along with the parameters themselves."

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